

(Offenlegung)

JP 02169800

(02)  
JP Patent Appln. Disclosure No. 169 800/90 - June 29, 1990

Patent Application No. 316 511/88 - Dec. 16, 1988

Applicants: Asahi Kasei Kogyo K.K., Osaka, Japan

Title: Latex for paper coating

Claim:

Latex for paper coating, which is a mixture of a polymer latex (A) and a polymer latex (B) as defined below, and in which the proportion of polymer latex (A) in said mixed latex is 40 to 90 weight-% on solid basis:

[ polymer latex (A) ]

Polymer latex synthesized from the monomers consisting of

- a. butadiene: 20 to 50 weight-%,
- b. ethylenically unsaturated carboxylic acid: 0.5 to 8 weight-%,
- and
- c. other monomers: 42 to 79.5 weight-%,

[ polymer latex (B) ]

Polymer latex synthesized from monomers consisting of

- a. alkyl acrylate: 20 to 50 weight-%,
- b. ethylenically unsaturated carboxylic acid: 0.5 to 8 weight-%,
- and
- c. other monomers: 42 to 79.5 weight-%,

wherein the particle size is in the range of 1500 to 6000 Å and the lowest film-forming temperature is in the range of 35 to 80°C.

### 3. Detailed Description of the Invention

#### ( Field of Application )

The present invention relates to a latex for paper coating and more particularly it provides a raw material for the preparation of a coated paper which has high white paper gloss and stiffness and also <sup>less</sup> ~~low~~ in inking unevenness in offset printing.

---

#### ( Prior Art )

A coated paper or a coated cardboard is prepared by applying an aqueous paint containing pigments such as kaolin clay, calcium carbonate, satin white, talc and titanium oxide; polymer latices as their binder; and water-soluble high polymers such as starch, polyvinyl alcohol, carboxymethylcellulose and casein as the water retention agents or assistant binders as the main constituents. <sup>to the surface of original papers</sup> The styrene-butadiene polymer latex prepared by emulsion-polymerizing styrene and butadiene as the main monomer components, so-called the SB latex has been widely used as ~~the polymer latex for a binder~~ <sup>for the polymer latex</sup>.

The production of coated papers has been recently remarkably increased as the demands of color printed magazines, pamphlets, advertisements and containers increase. Under such circumstances, there are high demands for more beautiful print finish and better printing workability and better touch. Among the coated paper qualities, high white paper gloss, even inking and improvement in stiffness are especially required. Thus,

slightly coated papers and lightly coated papers of low coating ( usually 5 to 10 g/m<sup>2</sup> on one side ) increased remarkably along the need for light weight in the coated paper. However, they are low in white paper gloss, compared to the common coated papers ( usually 10 to 20 g/m<sup>2</sup> on one side ) and tend to form inking unevenness in the printing and also is low in stiffness disadvantageously. The low white paper gloss and the formation of inking unevenness deteriorate largely the print finish. The low stiffness causes problems in printing workability and touch. The inking unevenness referred here means unevenness in ink trapping. In the offset color printing, 4 color inks of Indian ( black ), indigo, red and yellow are normally used and they are printed in this <sup>order</sup> ~~order~~. When the inks of second color and thereafter <sup>are</sup> ~~is~~ printed over the ink printed beforehand, the thickness of the ink transferred from the roll to the coated paper is varied from part to part and it is observed as unevenness. It is understood that such a phenomenon is caused by an uneven ink vehicle absorption according to structural unevenness of the coated paper surface.

Though the improvement in the SB latex as the paper coating binder has been investigated eagerly to solve the problem, no effective means has been found to date. It is because the white paper gloss of the coated paper, inking property and stiffness vary contrarily each other against the design factors

of the latex. For example, it is effective for the improvement in white paper gloss and inking unevenness to soften the polymer by increasing the ratio of butadiene as the latex polymer component, while it lowers stiffness. Contrary to it, when the ratio of butadiene is lowered to increase stiffness, white paper gloss is lowered and inking unevenness tends to occur and, in addition, ink pick resistance, that is ink pick strength, which is a fundamental requirement for coated paper is largely lowered to cause a new problem.

( Problems to be Solved )

Under such circumstances, we, inventors, provide a paper coating latex which can give a beautiful print finish of high white paper gloss and with no inking unevenness and which can produce coated papers in which printing workability and touch are improved by the high stiffness.

( Means for Solving the Problem )

The present invention provides a latex for paper coating which is a mixed latex of a polymer latex (A) and a polymer latex (B) mentioned below and in which the ratio of the polymer latex (A) in said mixed latex is 40 to 90 weight % on solid basis.

[ polymer latex (A) ]

A polymer latex synthesized from the monomers consisting of

- a. butadiene: 20 to 50 weight %.
- b. an ethylenically unsaturated carboxylic acid: 0.5 to 8 weight %

and

c. other monomers: 42 to 79.5 weight %.

[ polymer latex (B) ]

A polymer latex which is ~~a polymer latex~~ synthesized from the monomer components consisting of

a. an alkyl acrylate: 20 to 50 weight %,

b. an ethylenically unsaturated carboxylic acid: 0.5 to 8 weight %

and

c. other monomers: 42 to 79.5 weight %.

and in which the particle size is in the range of 1500 to 6000 Å and the lowest film-forming temperature is in the range of 35 to 80°C. The present invention will be illustrated in more details as follows.

Among the monomer components used for the synthesis of the polymer latex (A), butadiene <sup>must</sup> ~~shall~~ be in the range of 20 to 50 weight %. Within the range, the pick strength, a fundamental requirement for coated paper, can be maintained at a good level.

Thus, an amount lower than 20 weight % makes the polymer brittle, while an amount higher than 50 weight % makes the polymer too soft and poor in cohesion. In both cases, the pick strength cannot be exerted to a practical level. When the amount of butadiene is made lower than 20 weight %, stiffness is rather lowered due to the decrease in <sup>(fusion characteristics)</sup> cohesion of latex particles. Preferred amount of butadiene is in the range of 25

to 40 weight %.

The ethylenically unsaturated carboxylic acid is essential to maintain dispersion stability of the polymer latex and to fully exert the pick strength. The amount <sup>should</sup> ~~shall~~ be in the range of 0.5 to 8 weight %. An amount less than 0.5 weight % cannot maintain a high level of dispersion stability of the latex to cause various problems in the preparation of the paint and during coating. The pick strength cannot be also exerted. an amount higher than 8 weight % gives a too high viscosities ~~of~~ <sup>to</sup> the latex and the paint and water resistance is also deteriorated. Examples of the ethylenically unsaturated carboxylic acid include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid and crotonic acid.

The other monomers include, for example, aromatic vinyl compounds such as styrene,  $\alpha$ -methystyrene and vinyltoluene; alkyl methacrylates such as methyl methacrylate, ethyl methacrylate and butyl methacrylate; alkyl acrylates such as ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate; cyanovinyl compounds such as acrylonitrile and methacrylonitrile; and conjugated dienes such as isoprene and 2-chloro-1,3-butadiene.

Various other functional monomers can be contained, if required, usually in the range not higher than 10 weight %. They include, for example, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, acrylamide, methacrylamide,

N-methacrylamide, N-butoxymethylacrylamide and sodium styrenesulfonate.

Among the other monomers, styrene is used most typically and effectively. Methyl methacrylate and acrylonitrile come after it.

The particle size of the polymer latex (A) is not necessarily restricted in the present invention. However, the most preferred particle size of the latex used is in the range of 1000 to 2500 Å considered from the balance of the various quality and the physical properties.

Then, in the polymer latex (B), the acrylic ester <sup>should</sup> ~~shall~~ be in the range of 20 to 50 weight % of the monomer components. An amount lower than 20 weight % gives low pick strength and poor stiffness, while an amount higher than 50 weight % also gives poor stiffness.

The amount of the ethylenically unsaturated carboxylic acid <sup>(should)</sup> ~~shall~~ be in the range of 0.5 to 8 weight % <sup>for</sup> ~~the~~ the same reason as described for ~~the description of~~ the polymer latex (A).

The examples of the monomer are same as the examples of the polymer latex (A).

As the examples of other monomers, the same ones as described for the polymer latex (A) and a monomer most preferably used among them is styrene. Though butadiene can be used in addition to them if required, the addition of a monomer having two

double bonds in a molecule such as butadiene ~~shall~~ be restricted to a necessary minimum, usually 10 weight % or less. Otherwise, the effect of improving inking unevenness does not appear.

The polymer latex (B) <sup>must</sup> ~~shall~~ satisfy the above-mentioned requirement for monomer and, in addition, <sup>should</sup> ~~shall~~ have a particle size in the range of 1500 to 6000 Å and a lowest film-forming temperature in the range of 35 to 80 °C. A particle size smaller than 1500 Å hardly gives an effect of improving white paper gloss. A latex having a particle size <sup>larger</sup> ~~larger~~ than 6000 Å is difficult to be polymerized stably to give problem in manufacture. A lowest film-forming temperature lower than 35 °C shows no effect of improving white paper gloss and stiffness, while the temperature higher than 80 °C lowers the pick strength and shows no effect of improving stiffness. Preferred particle size and lowest film-forming temperature are respectively 1800 to 4000 Å and 45 to 70 °C.

The latex (A) and the latex (B) mentioned above are prepared by the known usual emulsion polymerization process. Thus, in a dispersion system containing water, a surface active agent, monomers and a radical polymerization catalyst as the basic constitution, the monomers are converted to an aqueous dispersion of polymer particles. The polymer concentration is generally in the range of 40 to 60 weight %. The surface active agents used include, for example, anionic surface active agents



such as fatty acid soap, rosin acid soap, alkylsulfonates, dialkylarylsulfonates, alkylsulfosuccinates, polyoxyethylene alkylsulfates and polyoxyethylene alkylarylsulfates; and nonionic surface active agents such as polyoxyethylene alkyl ethers, polyoxyethylene alkylaryl ethers, polyoxyethylene sorbitan fatty acid esters, and oxyethyleneoxypropylene block copolymers. An anionic surface active agent alone or a mixture of anionic and nonionic is usually used. The ratio to the monomers is generally in the range of 0.05 to 2 weight %. The latex particle size can be controlled by the ratio of the surface active agent used. Generally, a higher ratio gives a smaller particle size.

The polymerization catalyst causes addition polymerization of the monomers by being decomposed in the presence of heat or a reductive substance. Those which can be used include water-soluble or oil-soluble persulfates, peroxides and azobis compounds such as potassium persulfate, sodium persulfate, ammonium persulfate, hydrogen peroxide, t-butyl hydroperoxide, benzoyl peroxide, 2,2-azobisisobutyl<sup>o</sup>nitrile and cumene hydroperoxide. Most preferably used are persulfates. The ratio of the polymerization catalyst used is usually 0.2 to 1.5 weight % based on the monomers. The polymerization temperature is generally in the range of 60 to 90°C. When an increase in the polymerization velocity or a polymerization at a lower temperature is desired, so-called redox polymerization process

can be used in which a reducing agent such as sodium bisulfite, ascorbic acid or its salt, erysorbic acid or its salt and Rongalite is used in combination with the polymerization catalyst.

If required, various polymerization controllers are added in many cases. They include, for example, chain transfer agents for the control of polymer molecular weight and gel fraction such as carbon tetrachloride and mercaptans, pH adjusters such as caustic soda, potassium hydroxide, sodium hydrogen carbonate, sodium carbonate and disodium hydrogen phosphate, and various chelating agents such as sodium ethylenediaminetetraacetate.

The present invention provides a mixed latex of the polymer latex (A) and the polymer latex (B) and the ratio of the polymer latex (A) in said mixed latex <sup>should</sup> ~~shall~~ be 40 to 90 weight % on solid basis. A ratio lower than 40 weight % cannot keep the pick strength at sufficient level, while a ratio higher than 90 weight % cannot improve stiffness, white paper gloss and inking unevenness.

The latex according to the present invention can be used as a binder for the paper coating paint by a usual embodiment. Thus, the latex is mixed in water containing a dispersant <sup>dissolved-starch</sup> together with pigments, a water-soluble high polymer and various additives to prepare a uniform dispersion. The latex (A) and the latex (B) may be mixed beforehand or may be added separately during the preparation of the paint. The paint can be applied on an

*original paper*

cardboard by a usual method using a blade coater or a roll coater and so on. The latex according to the present invention can be naturally used usefully for the improvement of the quality of usual coated papers and coated cardboards in addition to slightly coated papers and lightly coated papers.

( Examples and Comparative Examples )

The present invention will be concretely illustrated by Examples and Comparative Examples as follows. Of course, the present invention is not restricted to the following Examples. The parts and the percentages shown below are based on weight.

(1) Preparation of the polymer latex

Specified amounts of water, a surface active agent and itaconic acid shown in the column of initial feed composition in Table 1 were fed to a pressure reaction vessel equipped with a stirring device and a jacket for temperature control and the inner temperature was raised to 80°C and then the monomer mixture and the aqueous catalyst solution shown in the Table were added at constant flow rates respectively over 5 and 6 hours. During the addition, the temperature was kept constant at 80°C. After the addition, the <sup>inner</sup> temperature was raised to <sup>95</sup>90°C and held at the temperature for 1 hour and then the mixture was ~~cooled~~ <sup>cooled</sup>. The polymer latex thus formed was adjusted to a pH of 7 with caustic soda and unreacted monomers were removed by steam stripping and the residue was filtered through a 200 mesh filter cloth. All

of the polymer latices were finally adjusted to a solid concentration of 50 % to be subjected to the following tests.

The particle sizes and ~~the~~ lowest film-forming temperatures of these polymer latices were measured by the following methods and the results are shown in Table 1.

Measurement of particle size:

The particle size of the polymer latex was measured by using a light scattering <sup>type</sup> particle size analyzer ( Model 6000 manufactured by C.N.Wood Co. ).

Measurement of lowest film-forming temperature:

It was measured in accordance with the following procedure by using a temperature gradient lowest film-forming temperature measuring equipment ( made by Takabayashi Rika Co. ) installed in a constant temperature <sup>and constant humidity</sup> room held at 23 °C and 65 % RH.

The latex was spread uniformly on an aluminum plate controlled to have a specified temperature gradient to ca. 100 microns thick and ca. 3 cm wide. The film-forming condition of the center part <sup>7.2cm width</sup> of the dried latex ~~of 2 cm wide~~ was observed and the lowest temperature at which no crack is formed was defined to be the lowest film-forming temperature of the latex.

(2) Examples and Comparative Examples

The performances of the polymer latices prepared by (1) were evaluated as the binders for paper coating. The coating

paint

paint was prepared by the composition shown in Table 2 and with a water amount to give a nonvolatile content of 55 % by using a high speed stirrer. The condition for the preparation of a coated paper by using the paint is shown in Table 3.

Table 2 Composition of the coating paint ( dry part by weight )

Additive	Amount added ( part )
Class 1 clay <sup>1)</sup>	80
<i>light</i> Precipitated calcium carbonate <sup>2)</sup>	20
Dispersant <sup>3)</sup>	0.3
Sodium pyrophosphate	0.1
Oxidized starch <sup>4)</sup>	10
Latex	10

( Note )

- 1) "Ultra White 90" manufactured by Engelhard Co.
- 2) "Tamapearl TP-222H" manufactured by Okutama Kogyo Co.
- 3) "Aron T-40" manufactured by Toa Gosei Kagaku Co.
- 4) "Oji Ace B" manufactured by Oji National Co.

Table 3 Condition for the preparation of coated papers

Raw paper to be coated	Medium quality raw paper, 60 g/m <sup>2</sup>
Coating machine	Bench gate roll coater
Coating speed	80 m/min
Drying condition	Hot air circulation 140 °C
Applied amount	Both sides. 8 g/cm <sup>2</sup> on one side
Super calender condition	

Machine type: Bench super calender manufactured by Yuri Roll

Kikai Co.

Temperature: 50°C

Pressure: 150 kg/cm<sup>2</sup>

Paper feeding frequency: Twice

White paper gloss, pick strength, inking unevenness and stiffness of the coated paper prepared were evaluated by the following methods.

White paper gloss:

It was measured by using Murakami's GM-26D Gloss Meter.

The incidence and reflection angles were 75°.

Pick strength:

Each 0.4 cc of a printing ink ( SD Super Delux 50 crimson B made by Toka Shikiso Co.; tack number 18 ) were printed 5 times by using an RI printing tester ( made by Akira Seisakusho Co. ) according to the usual method. The picking condition appeared on the rubber roll was transferred on another <sup>sheet</sup> ~~key sheet~~ and its condition was observed. The evaluation was carried out by 10 point evaluation method. Those of lower picking were given by a higher point.

Inking unevenness:

It was carried out by using an RI printing tester according to <sup>(a)</sup> trapping test method by the following procedure.

0.4 cc of yellow ink ( "TK New Bright G made by Toyo Ink

Co. ) was milled in No. 2 roll and 0.2 cc of crimson ink ( TK New Bright G made by Toyo Ink Co. ) was milled in No. 4 roll. Then, the ~~paper to be coated~~ <sup>coated paper</sup> was set on an impression cylinder and the first color was printed by the No. 2 roll and after 10 seconds the second color was printed by No. 4 roll. The printed coated paper was observed macroscopically and graded in the order of ◎, ○, △, × and ×× from the coating of small unevenness.

#### Stiffness:

By using a strip of coated paper specimen of 15 mm wide cut out to the paper-making direction, the limiting length was determined by a Clark stiffness tester ( made by Kumagaya Riki Co. ) according to the usual method. A higher value shows a higher stiffness.

Table 4 shows the test results of Examples, while Table 5 of Comparative Examples. As apparent from them, the coated papers prepared by using the latex of the present invention as the binder can be understood to be in <sup>excellent</sup> ~~high~~ balance between white paper gloss, pick strength, inking unevenness and stiffness.

Contrary to <sup>this</sup> ~~it~~, Comparative Examples were insufficient in any of the properties.

#### ( Effect of the Invention )

The latex for paper coating according to the present invention is useful for the preparation of a coated paper of high quality which maintains a sufficient pick strength and is high in

white paper gloss and stiffness and further low in inking unevenness.

Table 1

① Polymer latex classification ② Example latex (A)

③ Example latex (B) ④ Reference Example latex

⑤ Polymer latex No.

⑥ 1. Initial feed composition ( part )

Water

Surface active agent ( Note )

Itaconic acid

⑦ 2. Monomer mixture composition ( part )

Styrene

Methyl methacrylate

Acrylonitrile

Butadiene

Ethyl acrylate

Butyl acrylate

Carbon tetrachloride

t-Dodecylmercaptan

⑧ 3. Aqueous catalyst solution composition ( part )

Water

Surface active agent ( Note )

Caustic soda

Sodium persulfate



⑨ Property of the latex prepared

Particle size ( Å )

Lowest film-forming temperature (°C)

⑩ ( Note ) Surface active agent: 25 % aqueous solution of sodium alkylbenzenesulfonate

Table 4

① Example

② Latex composition

Latex (A)

Latex (B)

Mixing ratio (A)/(B)

③ Property of coated paper

White paper gloss ( % )

Dry pick strength

Inking unevenness

Stiffness ( mm )

Table 5

① Comparative Example

② Latex composition

Latex (A)

Latex (B)

Mixing ratio (A)/(B)

③ Property of coated paper

White paper gloss ( % )

Dry pick strength

Inking unevenness

Stiffness ( mm )

第1表

Table 1

Latex B

重合体ラテックス分類 ①	実施例ラテックス (A) ②			実施例ラテックス (B) ③			参考ラテックス ④		
重合体ラテックス No ⑤	a	b	c	d	e	f	g	h	i
1. 初期仕込組成 (部)									
水	70	70	70	70	70	70	70	70	70
界面活性剤 (注) ⑥	2.8	2.6	3.4	1.4	0.8	0.5	0.6	4.4	1.4
イタコン酸	2.0	2.5	2.5	2.0	2.0	2.5	2.5	2.0	2.0
2. 単量体混合物組成 (部)									
スチレン	42.0	38.5	34.5	58.0	60.0	57.5	55.5	56.0	38.0
メタクリル酸メチル	20.0	15.0	10.0	MMA--	10.0	--	20.0	--	10.0
アクリロニトリル	--	6.0	10.0	AN--	--	--	--	--	--
ブタジエン	36.0	27.0	43.0	BA--	--	--	22.0	--	--
アクリル酸エチル ⑦	--	5.0	--	EA 42	18.0	30.0	--	42.0	40.0
アクリル酸ブチル	--	--	--	BA--	10.0	10.0	--	--	10.0
四塩化炭素	8.0	6.0	8.0	CCl <sub>4</sub> --	--	--	6.0	--	--
ニードセルメルカプタン	--	--	0.1	Hex 0.2	0.2	0.2	--	0.2	0.2
3. 触媒水溶液組成 (部)									
水	28.6	28.6	28.6	28.6	28.6	28.6	28.6	28.6	28.6
界面活性剤 (注) ⑧	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
カセイソーダ	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
過硫酸ソーダ	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
調製ラテックスの性状 ⑨									
粒子径 (Å)	1750	1880	1610	2220	3000	3880	3290	1030	2370
最低成膜温度 (°C)	3	18	0	53	65	47	57	49	18

⑩ (注) 界面活性剤: アルキルベンゼンスルホン酸ソーダの25%水溶液

第4表 Table 4

	比較例 ①					
	1	2	3	4	5	6
ラテックス配合 ②						
ラテックス (A)	a	b	c	a	b	c
ラテックス (B)	d	f	e	e	d	f
(A) / (B) 混合比	60/40	80/20	50/50	70/30	70/30	80/40
竣工経水性 ③						
白濁光沢 (%)	55	49	62	53	46	66
ドライビック強度	8	8	8	9	9	10
インク着肉むら	○	○	○	○	○	○
スティフネス (mm)	143	150	146	145	152	140

第5表 Table 5

	比較例 ①						
	1	2	3	4	5	6	7
ラテックス配合 ②							
ラテックス (A)	a	b	c	--	g	a	a
ラテックス (B)	--	--	--	d	--	h	i
(A) / (B) 混合比	100/0	100/0	100/0	0/100	100/0	60/40	60/40
竣工経水性 ③							
白濁光沢 (%)	38	39	45	68	42	50	40
ドライビック強度	9	8	10	4	5	7	8
インク着肉むら	Δ	xx			xx	Δ	○
スティフネス (mm)	134	150	128	125	137	138	136

AN - 90-243088 [32]  
AP - JP880316511 881216  
PR - JP880316511 881216  
TI - Paper coating latex having high pick resistance - consisting of mixt.  
of butadiene and acid based latex, and acrylic based latex  
it - PAPER COATING LATEX HIGH PICK RESISTANCE CONSIST MIXTURE BUTADIENE  
ACID BASED LATEX ACRYLIC BASED LATEX  
PA - (ASAH ) ASahi CHEMICAL IND KK  
PN - ---JP2169800--- A 900629 DW9032  
ORD - 1990-06-29  
IC - D21H19/56  
FS - CPI  
DC - A82 F09 G02  
AB - J02169800 Paper coating latex consists of a mixt. of polymer latex  
(A) and polymer latex (B). The amt. of (A) is 40-90 wt.% of the mixt.  
on solid basis. (A) polymer latex is obtd. from 20-50 wt.% of  
butadiene, 0.5-8 wt.% of ethylenically unsatd. carboxylic acid, and  
42-79.5 wt.% of another monomer. (B) polymer latex is obtd. from 20-50  
wt.% of alkyl acrylate, 0.5-8 wt.% of ethylenically unsatd. carboxylic  
acid, and 42-79.5 wt.% of another monomer. (B) has particle size of  
1,500-6,000 angstrom and min. filing temp. of 35-80deg.C.  
- ADVANTAGE - The latex provides paper having high pick resistance,  
white paper gloss, and stiffness, and even ink transfer. (7pp  
Dwg.No.0/0)